Efficient optimization of nickel–cerium interface by constructing ethylene glycol ligand environment for fast water oxidation reaction kinetics

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ABSTRACT As a half-reaction to obtain high-efficiency and stable water-splitting, oxygen evolution reaction (OER) is a slow-kinetics process involving a four-electron ($4e^-$) transfer process and therefore requires catalysts to fasten electron transfer. Here, we rationally optimized an interface material of ceria nanoparticles and nickel hydroxide by adsorbing ethylene glycol (EG-Ni(OH)₂@CeO₂), which produced ultra-small nanosheets uniformly attached onto carbon cloth substrate. According to the characterization and density functional theory (DFT), the ethylene glycol-induced nickel–cerium interface had strong electron interaction, generating numerous of Ni^{(3-δ)+} active sites, reducing the energy reaction barrier, and promoting the electron-transport kinetics in the catalytic system. EG-Ni(OH)₂@CeO₂ showed excellent OER performance, with a low overpotential (335 mV) at 50 mA cm⁻² and a small Tafel slope (67.4 mV dec⁻¹). And the EG-Ni(OH)₂@CeO₂ also maintained stable for up to 60 h at 10, 20, and 30 mA cm⁻². Overall, this research shows the significance of the interface engineering of metal materials based on organic-solvent adsorption to improve the electrocatalytic OER process.

Keywords: ethylene-glycol ligand, nickel-cerium interface, Ni^{(3-δ)+}, oxygen evolution reaction

INTRODUCTION

The global energy crisis has sparked the research and development related to high-performance energy conversion and storage devices [1–6]. Electrocatalytic water splitting into hydrogen and oxygen is an attractive path

for developing sustainable energy [7–9]. However, the capacity of water splitting is severely restricted by the weak kinetics of the oxygen evolution reaction (OER) [10–13]. OER is a complicated process that involves a four-electron ($4e^-$) transfer and requires high oxygen evolution overpotentials and fast electron transfer rate [14–18]. Iridium oxide (IrO₂) and ruthenium oxide (RuO₂) have been known as the most active anodic semi-reactive OER catalysts of the electrocatalytic water splitting, but their scarcity and high cost largely limit their wide applications [19,20]. Thus, great efforts have been input toward ascertaining their non-precious alternatives.

The use of earth-abundant 3d metals as OER catalysts in place of noble metals has been proven suitable [21–24]. Among them, nickel oxide and nickel hydroxide exhibit promising OER activities but undergo weak electroconductivity [25–29]. Recently, some research teams reported significant improvement of the OER performance for oxygen generation *via* incorporating NiO and Ni(OH)₂ with impurity elements (namely, doping impurity elements [Fe [30], Co [31,32], Mo [33,34], and Ce [35,36]]) or constructing heterogeneous structures between impurity materials and Ni-based catalysts [37–39]. Zhao *et al.* [40] synthesized Ni_xCe_y@CP on carbon paper, in which the tight interface induced by the strong electron interaction between the interfaces involved the adjustment of the bond strength between the intermediate and the catalyst to enhance the conductivity of Ni(OH)₂. The distribution of ions and water at the interface would strongly affect the OER kinetic process and the electron

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transfer process [41].

Herein, we demonstrated a strategy that utilized unique ethylene-glycol (EG) ligand environments for efficient interfacial OER to enhance the kinetic catalysis. After being liganded by EG, the nickel-cerium (EG-Ni(OH)₂@CeO₂) nanosheets showed excellent OER performance with a low overpotential (335 mV) at 50 mA cm⁻² and a small Tafel slope (67.4 mV dec⁻¹). X-ray photoelectron spectroscopy (XPS) and electrochemical oxidation peaks indicated that the ethylene oxide-doped cerium oxide and nickel hydroxide formed a nanointerface, greatly increased the number of Ni^{(3-δ)+} active sites and the conversion of Ni²⁺ → Ni³⁺ during the electrochemical reaction, and consequently reduced the Tafel slope considerably and increased the rate of reaction kinetics. Density functional theory (DFT) demonstrated that the catalytic barrier was predicted to have optimally lowered down OER intermediates (OH*, O*, and OOH*) by forming the vast Ni^{(3-δ)+} site on EG-adsorbed nickel-cerium interface. Moreover, the EG-Ni(OH)₂@CeO₂ nanosheets had acceptable durability even after 60 h under 10, 20, and 30 mA cm⁻². The high OER performance manifests the importance of interface engineering according to organic-solvent adsorption in designing OER electrocatalysts.

EXPERIMENTAL SECTION

Chemicals and reagents

Nickel acetylacetonate (Ni(acac)₂), cerium nitrate (Ce(NO₃)₃), and *n*-butylamine (C₄H₁₁N) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Methanol (CH₃OH) was purchased from Xilong Scientific Co., LTD. Carbon cloth (CC) was purchased from Phychemi Hong Kong Company Limited. All reagents were used as-received without further purification.

Catalyst preparation

The typical synthesis of EG-Ni(OH)₂@CeO₂ was proceeded as follows. CC (2.5 cm × 2 cm) was sonicated in acetone, ethyl alcohol, and deionized water for 20 min and then dried for use. Next, 0.3 mmol of Ni(acac)₂ and 0.075 mmol of Ce(NO₃)₃·6H₂O were mixed in a solution (30 mL of methanol + 0.3 mL of *n*-butylamine) to form a suspension. The suspension and dry CC were ultrasonicated for 30 min, and then transferred to a 50-mL Teflon-linked steel autoclave heated up to 170°C for 10 h. Afterwards, the CC was rinsed thrice with ethyl alcohol and subsequently dried at room temperature for further use.

The prepared sample was placed in a three-necked flask

containing 100 mL of EG and reacted at 150°C for 12 min in an atmospheric pressure microwave (800 W), cooled to room temperature, and rinsed with ethanol to obtain EG-Ni(OH)₂@CeO₂. The synthesis of EG-Ni(OH)₂ was similar to that of EG-Ni(OH)₂@CeO₂ but without Ce (NO₃)₃·6H₂O. The mass loading of EG-Ni(OH)₂@CeO₂, Ni(OH)₂@CeO₂, and Ni(OH)₂ supported on CC were 0.64, 0.60, and 0.50 mg cm⁻², respectively.

In addition, we performed the following experiments for the synthesis of mw-Ni(OH)₂@CeO₂ without EG. The prepared Ni(OH)₂@CeO₂ sample was placed in a 100-mL microwave reaction vessel containing 80 mL of deionized water and treated with 800 W microwave in a dual-control (temperature and pressure control) microwave digestion apparatus at 150°C for 12 min. Upon cooling to room temperature, the finished CC was rinsed with ethanol to obtain mw-Ni(OH)₂@CeO₂.

Instrumentation and characterization

The microstructure of the catalysts was ascertained with a Hitachi S-4800 field emission scanning electron microscope (FESEM). The crystalline structure was identified using a D8 Tools X-ray diffraction (XRD) with a voltage of 40 kV and 30 mA as well as Cu-Kα radiation (λ=1.5406 Å). JEOL-2100F transmission electron microscopy (TEM) measurements were performed with an accelerating voltage of 120 kV. The atomic force microscope (AFM) was characterized by Seiko SPA400. Fourier transform infrared (FT-IR) spectra were conducted on a Bomem MB 100 FT-IR spectrometer in the wavenumber range between 400 and 4000 cm⁻¹. X-ray photoelectron spectroscopy (XPS) analyses of the material were conducted using a Thermo Electron Model with Al Kα as the excitation source.

Electrochemical measurements

The electrochemical performances of the materials toward OER were comprehensively evaluated with a traditional three-electrode electrolytic tank using the VMP-300 Electrochemical Workstation (Bio-Logic) in 1.0 mol L⁻¹ KOH. In this system, CC loaded with electrocatalyst was used as the working electrode, a saturated calomel electrode (SCE) was the reference electrode, and a Pt foil was employed as a counter electrode. Potentials were calibrated to a reversible hydrogen electrode (RHE) in Equation (1):

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.242\text{V} + 0.0592\text{pH}. \quad (1)$$

All currents presented in the graphs were normalized by the geometric surface area with 90% *iR* compensation. Tafel slopes were then procured from the corresponding

linear sweep voltammetry (LSV) and chronoamperometry (CP) with a multipotential step technique. The polarization curve was recorded at 5 mV s^{-1} from 0 to -0.7 V (vs. SCE). The stability test was performed in 1.0 mol L^{-1} KOH at 10, 20, and 30 mA cm^{-2} . Electrochemical impedance spectroscopy (EIS) was detected at 300 mV vs. RHE in a frequency range from 10^5 Hz to 0.1 MHz with an alternating current (AC) potential amplitude of 10 mV .

The turnover frequency (TOF) of the electrocatalytic reaction was estimated according to the amount of Ni in the materials using Equation (2):

$$\text{TOF} = (J \times A) / (4 \times F \times n), \quad (2)$$

where $J (\text{mA cm}^{-2})$ is the current density at a definite overpotential, $A (\text{cm}^2)$ is the surface area of the electrocatalysts (1 cm^2), 4 represents the 4 electrons to generate a mole of O_2 in OER, F is the Faraday's constant ($96,485 \text{ C mol}^{-1}$), and n is the number of moles of the electrochemical materials on the electrode.

Computational details

Calculations were realized in the DFT framework as implemented by the Vienna *Ab initio* Simulation Package (VASP) [42]. The exchange correlation functional was adopted employing generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) [43]. The slab models of $\text{Ni}(\text{OH})_2$ (101) and CeO_2 (220) had thickness of $12 \text{ \AA}$ and were divided by a vacuum zone of $20 \text{ \AA}$. The $\text{Ni}(\text{OH})_2$ (101)– CeO_2 (220) interface had an orthogonal lattice with a maximal lattice mismatch of 4%. $3 \times 3 \times 1$ K-points mesh with Monkhorst-Pack scheme was sampled in the Brillouin region. The structures were terminated when the force fulfilled $0.02 \text{ eV \AA}^{-1}$ and the iterative convergence of energy was set as 10^{-5} eV . The Gibbs free energy change (ΔG) of each reaction step was calculated as Equation (3):

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S, \quad (3)$$

where ΔE is the adsorption energy of reaction intermediates, and ΔZPE and ΔS are the zero-point energy and entropy change between the corresponding intermediates in the former state and the latter state, respectively.

RESULTS AND DISCUSSION

With respect to the synthesis of $\text{EG-Ni}(\text{OH})_2@\text{CeO}_2$ nanosheets (Fig. 1a). $\text{Ni}(\text{acac})_2$ and $\text{Ce}(\text{NO}_3)_3$ were initially added to the methanol solution containing *n*-butylamine, and the resulting solution was treated by hydrothermal reaction for 10 h. Then, microwave-assistant treatment was applied to the products for 12 min to produce the

$\text{EG-Ni}(\text{OH})_2@\text{CeO}_2$ nanosheets. The SEM image (Fig. S1) shows that the $\text{EG-Ni}(\text{OH})_2@\text{CeO}_2$ nanosheets (the size of 150 nm) were uniformly attached onto the CC substrate. AFM image shows the thickness of the ultrathin nanosheets of approximately 4.3 nm (Fig. 1b–d). The TEM (Fig. 1e) and particle size analysis (Fig. S2) indicate that the CeO_2 nanoparticles have a size of approximately 4 nm and are uniformly adhered to the $\text{Ni}(\text{OH})_2$ nanosheets. High resolution TEM (HRTEM) image (Fig. 2f) reveals that the CeO_2 with a 0.19 nm plane spacing corresponds to a (220) crystal face, whereas the $\text{Ni}(\text{OH})_2$ is in a polycrystalline state with chaotic short-lattice stripes (Fig. S3). Energy dispersive X-ray spectroscopy (EDS) mappings (Fig. 1g–j) show a uniform distribution of the Ni, Ce, and O in the $\text{EG-Ni}(\text{OH})_2@\text{CeO}_2$.

The chemical constitutions of the catalysts were characterized by XRD and FT-IR (Fig. 2). The peaks of $\text{Ni}(\text{OH})_2$ are indexed to the (003), (006), (101), (110) planes (JCPDS No. 38-0715). The peaks of 28.6° , 47.5° , and 56.3° of the CeO_2 crystal structure are according to the (111), (220), and (311) lattice planes (JCPDS No. 34-0394), respectively. Notably, the peak of $\text{EG-Ni}(\text{OH})_2@\text{CeO}_2$ left shifts approximately 1.1° due to the increasing of the interplanar spacing of (003) in comparison with $\text{Ni}(\text{OH})_2@\text{CeO}_2$. The reason is that the structure of the materials changes due to the adsorption of EG onto the surface of the sample during the microwave process. To verify the presence of EG in the sample, FT-IR was further introduced (Fig. 2b). After the EG treatment, the transmittance of the $-\text{CH}_2$ vibration, the O–H bending vibration, and C=O stretching vibration are significantly increased, demonstrating that EG [44] does exist in the $\text{EG-Ni}(\text{OH})_2@\text{CeO}_2$. Therefore, we prepared the $\text{EG-Ni}(\text{OH})_2@\text{CeO}_2$ via a facile way with less energy and time consumption.

The OER activities of different catalysts were evaluated in 1.0 mol L^{-1} KOH (Fig. 3). The small peak at $\sim 1.53 \text{ V}$ is ascribed to the formation of a small amount of Ni^{4+} during the OER process [45]. As expected, the OER activity of $\text{EG-Ni}(\text{OH})_2@\text{CeO}_2$ nanosheets is superior to that of IrO_2 . To reach 50 mA cm^{-2} , $\text{EG-Ni}(\text{OH})_2@\text{CeO}_2$ nanosheets merely require an overpotential of 335 mV , which is 181 mV less than that required by IrO_2 (Fig. 3c). Such overpotential is also 26 and 89 mV less than that of $\text{Ni}(\text{OH})_2@\text{CeO}_2$ and $\text{Ni}(\text{OH})_2$ (Table S1). The polarization curve per unit mass in Fig. S4 also shows that the $\text{EG-Ni}(\text{OH})_2@\text{CeO}_2$ has the best catalytic performance. Meanwhile, the OER performance of $\text{mw-Ni}(\text{OH})_2@\text{CeO}_2$ in Fig. S5 decreases, proving that EG has a positive effect on the OER process. Apparently, the $\text{EG-Ni}(\text{OH})_2@\text{CeO}_2$

Figure 1 (a) The synthesis of EG-Ni(OH)₂@CeO₂ nanosheets; (b–d) AFM images and the height profile; (e, f) TEM images; and (g–j) elemental mappings of Ni, Ce, and O of EG-Ni(OH)₂@CeO₂ nanosheets.

nanosheets possess the smallest Tafel slope (67.4 mV dec^{−1}), which is smaller than that of Ni(OH)₂@CeO₂ (91.1 mV dec^{−1}) and Ni(OH)₂ (138.9 mV dec^{−1}). Thus, the reaction kinetic rate of the nickel-cerium catalyst is greatly improved under the effect of EG (Fig. 3b). The Tafel slope of the EG-Ni(OH)₂@CeO₂ was further

evaluated by employing the steady-state polarization curves measured by CP (Fig. S6) [46]. The as-acquired Tafel slope of the EG-Ni(OH)₂@CeO₂ is 69.2 mV dec^{−1}, consistent with the value obtained by LSV. The Nyquist plots (Fig. 3d) reveal that the EG-Ni(OH)₂@CeO₂ nanosheets possess the lowest charge transfer resistance R_{ct}

Figure 2 (a) XRD patterns of Ni(OH)₂, Ni(OH)₂@CeO₂, and EG-Ni(OH)₂@CeO₂. (b) FT-IR spectra of Ni(OH)₂@CeO₂ and EG-Ni(OH)₂@CeO₂.

Figure 3 OER performance of the EG-Ni(OH)₂@CeO₂, Ni(OH)₂@CeO₂, and Ni(OH)₂. (a) LSV, (b) Tafel plots, (c) comparisons of Tafel slopes (top) and overpotentials at 50 mA cm⁻² (bottom), (d) fitted Nyquist plots with an equivalent circuit, (e) turnover frequency, and (f) CP curves at 10, 20, and 30 mA cm⁻².

of $2.427\ \Omega$ among all catalysts. The small R_{ct} values also indicate the fast electron transfer kinetics rate and enhanced conductivity. The TOF associated with Ni is 0.04, 0.09 and $0.2\ \text{s}^{-1}$ at the overpotentials of 300, 350 and 400 mV, respectively (Fig. 3e). The calculated Faradaic efficiency of the EG-Ni(OH)₂@CeO₂ is 98% for OER in $1.0\ \text{mol L}^{-1}$ KOH (Fig. S7). Stability is an indispensable feature for a comparable catalyst. The long-time stability test was conducted at 10, 20, and $30\ \text{mA cm}^{-2}$ (Fig. 3f). The potential loss under these current densities can be negligible after 60 h. Moreover, little morphology and structure changes (Figs S8–S11) were observed after 20 h under $10\ \text{mA cm}^{-2}$, suggesting the comparable stability of the EG-Ni(OH)₂@CeO₂ nanosheets. Meanwhile, Fig. S12 shows that the residual EG during OER process is stable.

To investigate the OER mechanism on EG-Ni(OH)₂@CeO₂ nanosheets, XPS was used to analyze the surface electron states of the EG-Ni(OH)₂@CeO₂. The elemental composition of EG-Ni(OH)₂@CeO₂, including Ni, Ce, and O, was further confirmed by using full measurement scan XPS spectra (Fig. S13). Compared with Ni(OH)₂, the Ni 2p spectrum of Ni(OH)₂@CeO₂ shifts $\sim 0.18\ \text{eV}$ to the lower binding energy (Fig. 4a) and corresponds to the change of the chemical state of Ni from a high-valence

(Ni³⁺) to a low-valence state (Ni^{(3-δ)+}), thereby indicating a strong electron interaction between Ni(OH)₂ and CeO₂ [47]. Then the presence of EG ligand lowers the calculated molar ratio of Ni²⁺/Ni³⁺ from 1.4 to 0.87 (Fig. 4c, blue). This result suggests that the EG-Ni(OH)₂@CeO₂ has the highest Ni³⁺ concentration and the nickel-cerium interface is further optimized to produce more Ni^{(3-δ)+} active sites under the EG environment, consequently facilitating the rapid progress of the OER reaction. Hence, the adsorption of EG leads to a decrease in the ratio of Ni²⁺/Ni³⁺ in Ni(OH)₂, the ionic radius of Ni³⁺ is smaller than that of Ni²⁺ and the interplanar spacing of (003) increases, which is consistent with the XRD results (Fig. 2a). The Ce consists of 3d_{5/2} and 3d_{3/2} spin-orbit [48] (Fig. 4b). The Ce 3d spectra were fitted into eight peaks, and the change in the peak area revealed that the Ce³⁺ concentration greatly increased after EG treatment. Concretely, the calculated molar ratio of Ce³⁺/Ce⁴⁺ changes from 0.83 to 1.46 according to the v'/v'' and u'/u'' (Fig. 4c, red). Combined with O 1s spectra of Ni(OH)₂@CeO₂, Ni(OH)₂, and CeO₂ before and after EG treatment, the Ce–O peak at $\sim 529.5\ \text{eV}$ was weakened in Ni(OH)₂@CeO₂ and CeO₂ after EG treatment, and no significant metal-oxygen peak was found in Ni(OH)₂

Figure 4 (a) Ni 2p XPS spectra of EG-Ni(OH)₂@CeO₂, Ni(OH)₂@CeO₂, and Ni(OH)₂; (b) Ce 3d XPS spectra of EG-Ni(OH)₂@CeO₂, Ni(OH)₂@CeO₂, and CeO₂; (c) molar ratios of Ce³⁺/Ce⁴⁺ (red) of the EG-Ni(OH)₂@CeO₂, Ni(OH)₂@CeO₂ and molar ratios of Ni²⁺/Ni³⁺ (blue) of the EG-Ni(OH)₂@CeO₂, Ni(OH)₂@CeO₂, Ni(OH)₂; (d) O 1s XPS of different catalysts.

(Fig. 4d) [49]. EG was preferentially adsorbed onto the CeO_2 , thereby affecting the electronic state of the CeO_2 from Ce^{4+} to Ce^{3+} , and further increasing the concentration of $\text{Ni}^{(3-\delta)+}$ in the $\text{EG-Ni(OH)}_2@/\text{CeO}_2$ via electron transport effect.

To further understand the intrinsic effect, the electrocatalytic processes were studied to check the interfacial effect on the OER. The four main sequential steps of OER in alkaline conditions were explored [50]:

where $*$ represents the element of the surface reaction sites. For the Ni-base catalysts, Ni^{3+} is commonly considered to be the most catalytic site in the OER process [40,51]. However, Ni^{3+} has a strong adsorption capacity for O^* and is not conducive to the continued production of OOH^* [52,53]. So the potential determining step (PDS) occurs at the intermediate O^* species. The construction of the nickel-cerium interface results in electron transfer from cerium to nickel to produce $\text{Ni}^{(3-\delta)+}$ at the interface, and such transfer is beneficial for weakening the

adsorption of the Ni site to the O^* intermediate. For the electrocatalytic water oxidation, one obvious oxidation process attributed to the $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+}$ (ca. 1.37 V vs. RHE in Fig. 5a) in the cyclic voltammetry (CV) plots was detected. Note that increased oxidation peak current due to the adsorption of the EG ligand results in the conversion of more Ni^{2+} to Ni^{3+} in the electrochemical reaction of the $\text{EG-Ni(OH)}_2@/\text{CeO}_2$, and this development is more favorable for the OER catalytic reaction.

DFT calculations were also implemented to further examine the microscopic mechanism of OER enhancement on the $\text{EG-Ni(OH)}_2@/\text{CeO}_2$. The optimized structures of the $\text{EG-Ni(OH)}_2@/\text{CeO}_2$, $\text{Ni(OH)}_2@/\text{CeO}_2$, and Ni(OH)_2 were presented in Figs S14–S16, respectively. A reaction mechanism is depicted in Fig. 5c. In the case of $\text{EG-Ni(OH)}_2@/\text{CeO}_2$, one free hydroxide ion was adsorbed onto the exposed Ni site, and proceeded through the formation of OH^* , O^* , and OOH^* intermediates and finally accelerated the O_2 production. From the view on free-energy changes of the intermediates for different catalysts, the energy-change lines under the catalytic roles of the $\text{EG-Ni(OH)}_2@/\text{CeO}_2$ showed that the free-energy barriers of the $\text{EG-Ni(OH)}_2@/\text{CeO}_2$ was much lower than

Figure 5 (a) Oxidation peak of the CV curves; (b) free energy diagram for OER of the $\text{EG-Ni(OH)}_2@/\text{CeO}_2$, $\text{Ni(OH)}_2@/\text{CeO}_2$, and Ni(OH)_2 . (c) Proposed mechanism of O_2 evolution over the $\text{EG-Ni(OH)}_2@/\text{CeO}_2$.

that of $\text{Ni}(\text{OH})_2@ \text{CeO}_2$ and $\text{Ni}(\text{OH})_2$ (Fig. 5b). Specifically, the barriers of O^* intermediate PDS are 0.55, 0.62, and 4.21 eV for $\text{EG-Ni}(\text{OH})_2@ \text{CeO}_2$, $\text{Ni}(\text{OH})_2@ \text{CeO}_2$, and $\text{Ni}(\text{OH})_2$, respectively. Thus, the $\text{EG-Ni}(\text{OH})_2@ \text{CeO}_2$ has the lowest energy reaction barrier and the fastest reaction kinetic rate.

Given the above DFT calculations and control experiments, doping EG-adsorbed CeO_2 reduces the reaction barrier in the entire OER reaction. During this process, the mechanism of EG-adsorbed CeO_2 optimized the electronic valence of the Ni site and the OER performance of the $\text{EG-Ni}(\text{OH})_2@ \text{CeO}_2$ was improved (Fig. 6). On the basis of the presence of $\text{Ni}^{(3-\delta)+}$ at the nickel-ceria interface, the amount of $\text{Ni}^{(3-\delta)+}$ active sites was increased by adsorbing EG ligands, increasing the overall kinetic rate of the OER catalytic reaction. Therefore, the OER electrocatalytic activity of nickel hydroxide nanosheets is improved by the tuning of the EG-adsorbed CeO_2 .

CONCLUSION

To sum up, the novel material $\text{EG-Ni}(\text{OH})_2@ \text{CeO}_2$ grown on CC was developed and used as high-efficiency catalysts for OER. The $\text{EG-Ni}(\text{OH})_2@ \text{CeO}_2$ enabled high performance with a low overpotential (335 mV) to reach 50 mA cm^{-2} , a Tafel slope (67.4 mV dec^{-1}) and compar-

able long-term durability toward OER. Characterization and theoretical calculations confirmed that the excellent performance of $\text{EG-Ni}(\text{OH})_2@ \text{CeO}_2$ could be attributed to EG-adsorbed CeO_2 controlling the electronic state of $\text{Ni}(\text{OH})_2$, which greatly increased the concentration of $\text{Ni}^{(3-\delta)+}$ and reduced the reaction barrier in the OER catalytic process. This work reveals the effect of EG ligands on the catalytic interface, and provides some inspiration for interface material construction under an organic ligand environment.

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Figure 6 OER processes with different catalysts: (a) $\text{Ni}(\text{OH})_2$, (b) $\text{Ni}(\text{OH})_2@ \text{CeO}_2$, and (c) $\text{EG-Ni}(\text{OH})_2@ \text{CeO}_2$.

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Supplementary information Experimental details and supporting data are available in the online version of the paper.

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通过构建乙二醇配体环境有效优化镍-铈界面以加速水氧化反应动力学

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摘要 析氧反应(OER)作为获得高效稳定水裂解的半反应, 是一个涉及四电子($4e^-$)转移过程的缓慢动力学过程, 因此需要催化剂加快电子转移速率以促进反应进行. 本文利用乙二醇配体的吸附作用优化二氧化铈纳米颗粒和氢氧化镍纳米片构建的界面材料(EG-Ni(OH)₂@CeO₂). 分析表征和密度泛函理论(DFT)证明, 乙二醇诱导的镍-铈界面具有很强的电子相互作用, 产生了大量的Ni^{(3-δ)+}活性位点, 降低了反应势垒, 并促进了催化体系中的电子传输动力学. EG-Ni(OH)₂@CeO₂具有出色的OER性能, 在50 mA cm⁻²下表现出335 mV的过电位和67.4 mV dec⁻¹的Tafel斜率. 在10、20和30 mA cm⁻²下可保持60 h稳定. 本研究表明基于有机溶剂吸附的金属界面工程对改善电催化OER工艺的重要性.